

Solubilities of Salen Derivatives and Their Cobalt Complex in Liquid and Supercritical CO₂

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The solubility of N,N'-Bis(salicylidene) ethylenediamine (*n*-salen) and N,N'-bis(3,5-di-*tert*-butylsalicylidene) ethylenediamine (*t*-butyl-salen) was studied with *in-situ* UV-VIS spectrometer. *n*-Salen is 3-5 times more soluble than *t*-butyl-salen in liquid or supercritical CO₂. This behavior may be attributed to Lewis acid-base interaction between salen and CO₂. The chelation of salen with Co²⁺ ion in supercritical condition was confirmed to be fast enough above room temperature. However, the metal ion extraction capability of *t*-butyl salen is relatively poor because of its low solubility and ionic nature of complex.

Key Words : Solubility, Salen, Supercritical CO₂, Fiber optics

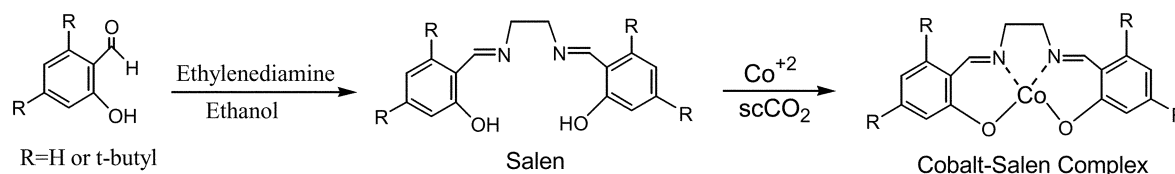
Introduction

The potential usages of carbon dioxide (CO₂) as an environmentally benign solvent have been realized on many commercial applications¹⁻³ such as food process, cleaning protocol in microelectronics and dry-cleaning industries, nuclear waste extraction. Supercritical CO₂ (sc-CO₂) modified by the addition of the complexing agent has been utilized in the extraction of metal ions from various solid and liquid matrices.^{4,5} In order to be successful supercritical fluid extraction (SFE) of metal ions, several important requirements exist such as high formation constant of metal complexes, fast kinetics, and good solubility and stability of both the chelating agent and the metal chelate in supercritical fluid. Various chelating agents, such as dithiocarbamates, β-diketones, crown ethers, and organophosphorous compounds have been used for extracting metal species in supercritical CO₂.^{6,7} Nevertheless, many chelating agents have drawbacks and problems relating to metal ion extraction in CO₂, *i.e.*, poor stability and solubility, and material cost. In order to overcome these problems, new effective chelating agent must be designed and selected. For this purpose, N,N'-bis(salicylidene) ethylenediamine (*n*-salen) has been suggested as a new chelating agent of metal ions in sc-CO₂ because of easy synthesis and its well-known metal complex.^{8,9} In this study, solubility and reactivity of two salen derivatives and their metal complex in liquid or supercritical CO₂ were investigated for the extraction of metal ions.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used as received except salen derivatives. Commercial grade and 99.99% CO₂ gases were used for CO₂ experiment. N,N'-Bis(salicylidene) ethylenediamine (*n*-salen) and N,N'-bis(3,5-di-*tert*-butylsalicylidene) ethylenediamine (*t*-butyl-salen) were synthesized by the literature procedure.^{8,9} The procedure is summarized in Scheme 1. Ethylenediamine (8.3 mmol) was added drop-wise to 2-hydroxybenzaldehyde (16.6 mmol) in fresh distilled 12 mL ethanol and the solution was refluxed for 2 hours under stirring. Yellow precipitate was filtered and washed with cold methanol. The resulting *n*-salen was recrystallized in ethylacetate/hexane and dried. *t*-Butyl-salen was synthesized similarly with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. Cobalt complex (*t*-butyl-salen-Co) was easily made in hot methanol with Co(NO₃)₂·6H₂O and *t*-butyl-salen.

Apparatus and Sample Preparations. The apparatus used in this experiment was designed by Hunt *et al.*¹⁰ and was summarized in Figure 1. It can be operated up to 300 bar of pressure and temperature from ambient to 100 °C. The syringe pump (ISCO Model 260D, U.S.A.) was used to deliver CO₂ to the reactor cell, and control and monitor the operating pressure with the accuracy of 0.1 bar. Using the external pressure gauge (Keller, Model Leo-2, Swiss), the pressure monitor of the syringe pump and pressure transducer were recalibrated. To control the reactor cell temper-



Scheme 1

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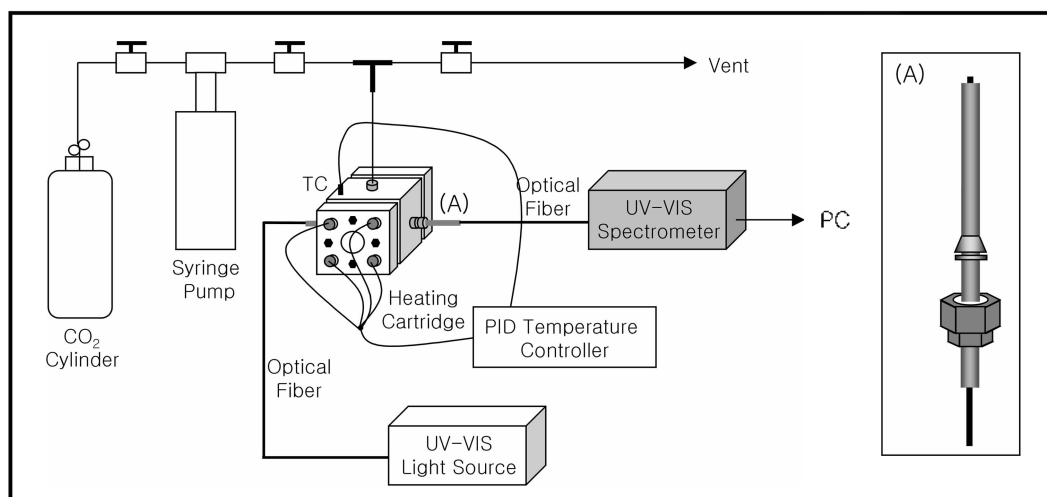


Figure 1. Schematics of high pressure reactor cell with optical fibers for UV-VIS measurement. Inset shown is the details of the fiber coupler with a PEEK tubing and fittings.

ature, home-built temperature controller was used. With 4 heating cartridges (Omega, U.S.A.), thermocouple and PID controller (Hanyang, Korea), the reactor cell temperature can be controlled and maintained within 0.1 °C accuracy. The 58 × 58 × 58 mm vessel block with 15 mm diameter hollow cylinder was machined from type 316 stainless steel. To achieve the sealing of the view ports, Teflon gaskets were lined on the body of the reaction vessel and 7 mm sapphire window at each end was bolted down to the body of reaction vessel using another piece of stainless steel block with a 15 mm diameter opening. Two 1/16 inch holes to the middle of cell were precisely drilled in an aligned manner at the right angle of the hollow cylinder and were machined to accept 1/16 inch male connectors in order to fit optical fibers as shown in Figure 1(A). One end of the each fiber with SMA906 connector connected to the CCD array UV-VIS spectrometer (Avantest AVS-USB2000) or UV-VIS source (Avantest DH-2000) and the other end was inserted into the cell through 1/16 inch PEEK tubing and ferrule fitting as shown in Figure 1(A). Once the ferrule was set at the particular length from the end of fiber, the optical path-length between the pair of fibers was fixed. Since the concentration range of the materials under study may be very large, several optical fiber pairs with different path-lengths were prepared. In this experiment, 5 different optical fibers were prepared so that the path lengths between the inserted fibers could be varied from 1 mm to 15 mm. UV-VIS spectra were obtained by a given path-length optical fiber pair inserted into the cell and the path-length was calibrated with known concentrations. 4 different *n*-salen solutions of known concentrations in hexane were prepared to calibrate the path-length between the mounted fibers. The comparison between the measured UV absorbance of the solutions with regular UV-VIS spectrometer and fiber-optics UV-VIS spectrometer gave the path-length between optical fibers. From the absorbance vs. concentration plot of solutions, the ratio of the slopes between two sets of measurements gave the path-length of a given fiber pairs. With this method,

the accuracy of path-length was confirmed to be better than 5%. Due to the fiber-optics cut-off below 250 nm, however, peaks below the limit cannot be observed. With this type of reactor cell, *in-situ* UV-VIS spectrum and cell reaction process can be easily monitored. The amount of metal ions after extraction was analyzed by ICP method (LEEMAN ABS Inc., Model DRE SPEC).

To test the solubility, the known concentration solution of salen was prepared in methanol and excess amount of the solution was added to the vessel and the solvent was evaporated. Upon adding the CO₂, the concentration and the solubility of a given salen was calculated based on the absorbance of UV-VIS spectra. In order to obtain the equilibrium solubility at given pressure and temperature, *in-situ* absorbance of salen in CO₂ fluid was monitored until no further change in the absorbance occurred. Its equilibrium absorbance was measured at another 30 min later and its equilibrium solubility was determined. For cobalt ion extraction, 1 cm × 1 cm filter paper (Whatmann No. 2) was used as a substrate. With 1000 ppm Co²⁺ ion standard solution, 1.60 ppm sample specimen for Co²⁺ ion extraction was prepared. After Co²⁺ ion extraction experiment, ICP analysis was followed after the acid digestion with HNO₃ and the reported extraction efficiency was calculated from the ICP result.

Results and Discussions

Figures 2 and 3 show *in-situ* UV-VIS spectra of *n*-salen and *t*-butyl-salen, respectively. Both salen derivatives dissolve gradually up to a few mM order as CO₂ pressure increases. Normally, salen derivatives have another peak below 270 nm which is not shown in Figures 2 and 3 due to the fiber-optics cut-off. The peak between 280 nm and 380 nm was used to calculate the concentration of salen in either liquid or supercritical CO₂. The solubility of two salen derivatives at 21 °C and 61 °C are summarized in Figure 4. In liquid CO₂ at 21 °C, *n*-salen dissolves 5 times more than *t*-butyl salen.

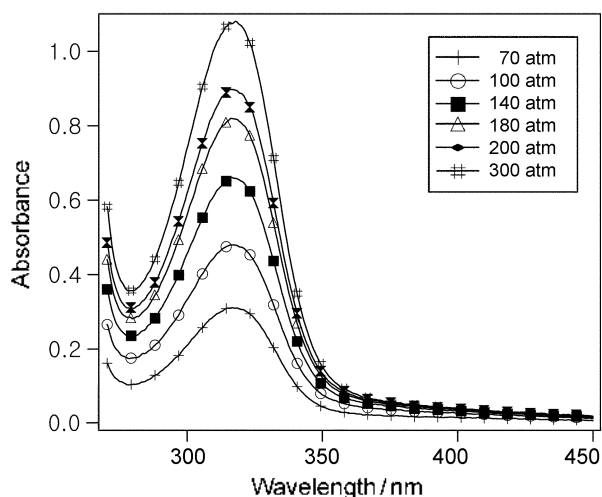


Figure 2. UV-VIS spectra of *n*-salen as function of CO₂ pressure at 21 °C.

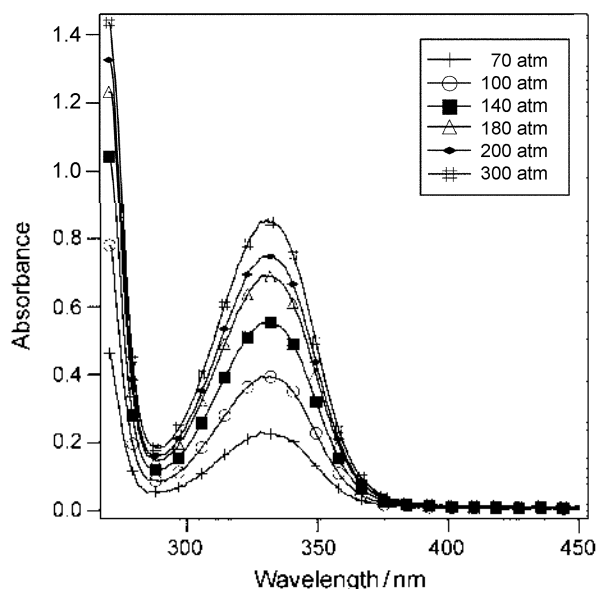


Figure 3. UV-VIS spectra of *t*-butyl-salen as function of CO₂ pressure at 21 °C.

Considering *n*-salen is sparingly soluble in hexane whereas *t*-butyl salen dissolves rather well, it is rather surprising that the solubility of *n*-salen in CO₂ solvent is better than that of *t*-butyl salen. Perhaps, this may be due to Lewis acid-base interaction between salen and CO₂. However, in the case of *t*-butyl-salen, because its four *t*-butyl groups may prevent the acid-base interaction, its solubility is less compared to *n*-salen. At 61 °C, *t*-butyl salen rarely dissolves below 100 bar and from 180 bar its solubility surpasses that of liquid state mainly due to the density difference as pressure increases.

Complex formation of salen derivatives were reported in many literatures^{9,11-13} and it was confirmed using methanol solution of salen derivatives and Co(NO₃)₂ in this laboratory. However, the solubility of salen-complex derivatives in liquid and supercritical CO₂ is little known and recently it was reported that *n*-salen complex is not soluble in sc-

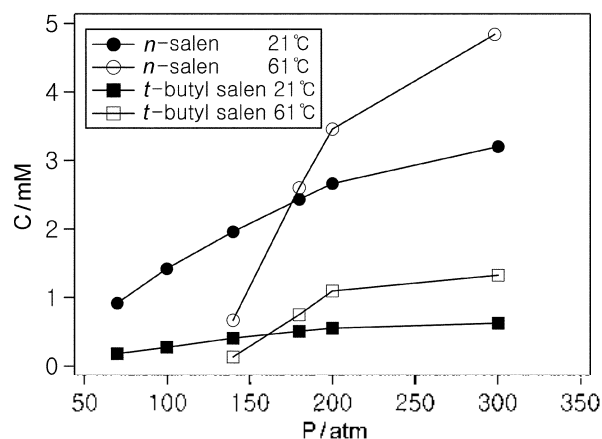


Figure 4. The solubility of *n*-salen and *t*-butyl-salen at various pressures.

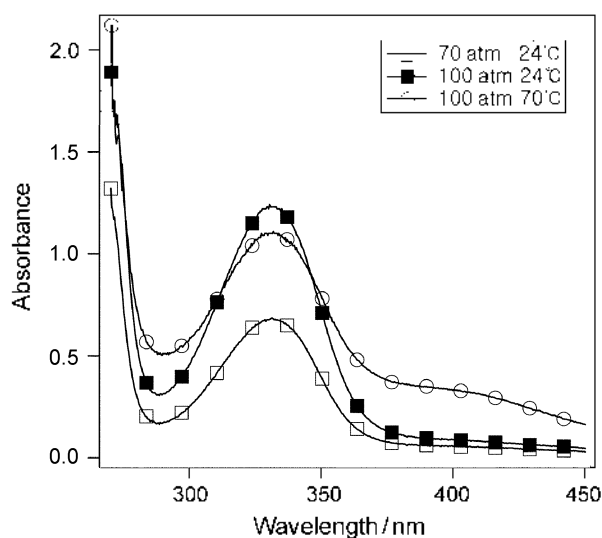


Figure 5. *t*-Butyl salen-Co^{II} complex formation with the concentration ratio of Co²⁺/salen = 1.

CO₂.¹⁴ In order to test the complex formation of *t*-butyl salen with Co²⁺ ion, the sample was prepared as follows: the known amount of Co(NO₃)₂ in methanol was added to the reaction vessel and the solvent was evaporated. Also, the calculated amount of solid *t*-butyl salen was added to the reaction vessel. Since the purpose of this experiment is to confirm the complex formation using *in-situ* UV-VIS, the possible Co(NO₃)₂ loss during heating or residual methanol were not checked.

As shown in Figure 5, CO₂ fluid was added into the cell and the absorbance peak of *t*-butyl salen at 330 nm appeared at 70 bar. At 24 °C, no complex formation with Co²⁺ ion was observed even at the pressure of 100 bar indicating that the complex formation kinetics is slow at this temperature. At 70 °C, however, new peak around 400 nm was confirmed to be originated from *t*-butyl-salen-Co complex. When an excess amount of Co²⁺ ion was used, clean *t*-butyl-salen-Co peak around 390 nm is observed as shown in Figure 5 and free *t*-butyl-salen peak at 330 nm completely disappeared because of its complexation with Co²⁺ ion.

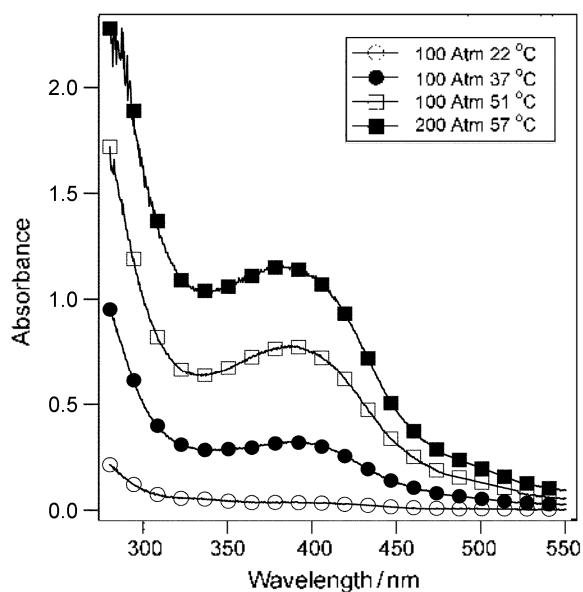


Figure 6. *t*-Butyl salen- Co^{+1} complex formation with the concentration ratio of $\text{Co}^{+1}/\text{salen} = 20$. No free *t*-butyl-salen peak at 330 nm is observed.

Since *t*-butyl salen can form a complex with cobalt ion in supercritical CO_2 , it may be used as an extracting material for the supercritical CO_2 metal extraction. With a filter paper containing 1.60 ppm Co^{+1} ion, the extraction ability of *t*-butyl salen was tested. Without any modifier such as water or methanol to increase the extraction ability of salen, no cobalt ion extraction was observed, indicating *t*-butyl-salen alone does not have an ion solvating power or/and the substrate have a strong adhesion force toward metal ion. In order to increase solvating power of CO_2 toward metal ions, methanol has been used as solvent modifier and is very soluble with CO_2 fluid. In many applications, in fact, 5% methanol added CO_2 has commonly been used. As shown in Figure 6, with 20 or 200 μL methanol damped specimens, Co^{+1} ion was statically extracted from the filter paper substrate for 1 hour. Since methanol modified CO_2 can extract the metal ion, the extraction efficiency of methanol itself was checked with the same experimental condition without any salen. It was found to be about 40% extraction efficiency with 200 μL methanol modified CO_2 fluid. All efficiency shown in Figure 7 with *t*-butyl-salen/200 ml methanol modified CO_2 fluid is above 60% but it is not quite a promising result. However, this result is understandable. The solubility of *t*-butyl salen itself is about order of 1 mM in either liquid or supercritical CO_2 . Once it is chelated with Co^{+1} ion, the solubility of *t*-butyl salen- Co^{+1} complex will decrease substantially because of its ionic nature. To overcome this problem, more CO_2 -phillic group of salen moiety and the CO_2 -soluble compensating counter ion must be introduced. Further studies of salen derivatives with CO_2 -phillic group will be reported.

Conclusion

The solubility of *n*-salen and *t*-butyl-salen in liquid/

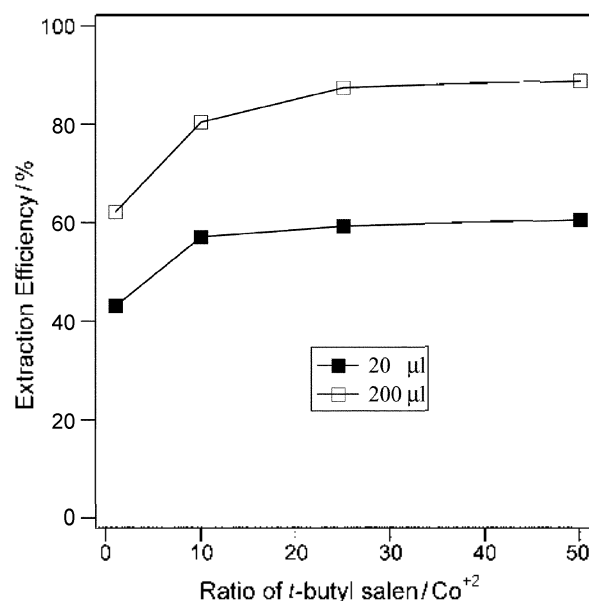


Figure 7. Co^{+2} ion extraction efficiency of *t*-butyl-salen with 20 and 200 μL methanol damped specimens.

supercritical CO_2 was studied with *in-situ* UV-VIS spectrometer. Unexpectedly, *n*-salen is 3-5 times more soluble than *t*-butyl-salen in liquid or supercritical CO_2 . This behavior may be attributed to Lewis acid-base interaction between salen and CO_2 and bulky *t*-butyl groups in *t*-butyl-salen hinder the acid-base interaction so that its solubility is less. The chelation of salen with Co^{+1} ion in supercritical condition was confirmed. However, the metal ion extraction capability of *t*-butyl-salen is poor because of its low solubility and ionic nature when the chelation occurs

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